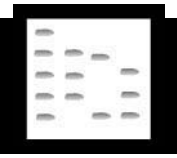
PARTICULATE CHARACTERIZATION: INVERSE GAS CHROMATOGRAPHY



D. Butler and D. R. Williams, Surface Measurement Systems, London, UK

Copyright © 2000 Academic Press

Introduction

Inverse gas chromatography (IGC) represents a unique refinement of a classic chromatographic method in which an unknown solid material such as a powder, fibre or film may be characterized. By reversing the traditional role of unknown mobile phases and known reference stationary phases, the gas–solid chromatographic retention processes may be used to characterize an unknown particulate sample by eluting a series of known gas or vapour molecules through a column packed with the sample materials. IGC is the only chromatographic technique in which a solid-state material may be characterized in its native state. Despite the fact that over 500 papers have been published over the last 8 years using IGC, the technique is still not well known nor well appreciated by many scientists. However, this article will highlight the opportunities that IGC offers for surface and materials characterization generally as well as briefly reviewing the principles and main IGC methodologies. Finally, recent trends in material characterization applications will be briefly reviewed.

DropBooks

History

The intrinsic relationship between gas–solid chromatography and the adsorption isotherm was established by a number of workers starting in the 1940s and going through the 1950s. Gluckauf, Martin, James, Gregg, Purnell, Wilson, Wicke and Stock all contributed to our early understanding of gas–solid chromatographic retention/adsorption processes which forms the basis of analytical gas chromatography (GC) as we know it today.

The first systematic use of GC as a technique for characterizing solid-state materials was pioneered by Russian scientists in the early 1960s led by Professor Kiselev at Moscow University who also coined the terminology IGC. Their work was motivated by an interest in understanding the fundamental nature of gas–solid retention behaviour for high energy solid surfaces including carbons, zeolites, silica, alumina and catalyst materials as well as other porous solids. Their work resulted in a very detailed fundamental understanding of the gas-phase adsorption processes on these particulate materials which were additionally being evaluated as stationary phases for traditional analytical chromatography. Their work allowed a detailed understanding of the adsorption processes including heats of adsorption, diffusion processes, adsorption processes, specific surface interactions and surface areas. Work was undertaken at both low and high solute concentrations.

Through the 1960s and 1970s research activity on IGC moved on to other classes of materials for study, most notably polymers. New refinements in both experimental technique as well as data analysis were pioneered. Many studies of polymer glass transition temperatures, small molecule diffusion, polymer–polymer interactions and crystallinity were first reported in this period. Workers such as Guillet, Conder, Smidsrod, Laub, Schrieber and Gray were all productive during this period.

During the 1980s and 1990s we have seen a much wider range of materials being studied using IGC. Initially this commenced with surface studies on fibres and filler particles for advanced materials, and more recently we have seen growing interest in IGC for food and pharmaceutical characterization. Techniques have remained very much unchanged during this period with virtually all work published being based on low solute concentrations. Refined analyses have been developed to determine the surface energy and acid–base properties of particulate materials as well as methods for determining polymer–polymer interaction constants and solubility parameters. Workers including Gray, Lawrence, Duda, Papirer, Schultz, Balard, Munk, DiPaola-Baranyi have all published significant work during this period. The recent availability of commercial IGC equipment which can perform a wide new range of experimental IGC methods is certain to catalyse growth in this technique in the new millennium.

Instrumentation

Virtually all of the published work on IGC has been undertaken on either home-built or modified commercial GC equipment. Though both analytical and physicochemical measurement approaches such as IGC are intrinsically very similar, the demands for

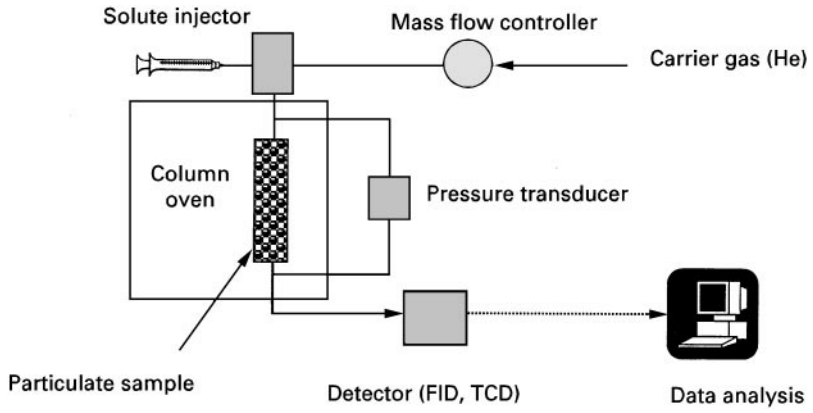


Figure 1 Typical schematic of an IGC system for infinite dilution studies. FID, Flame ionization detector; TCD, thermal conductivity detector.

accurate and precise retention data for physicochemical measurement have required additional experimental refinement not normal nor standard for analytical GC equipment.

Ideally, well-designed IGC equipment for low solute concentrations should incorporate:

1. thermal conductivity mass flow controllers
2. pressure sensors for measuring pressure drop along the column
3. computerized data acquisition of detector signals
4. full statistical analysis of solute peak/boundary shapes

Figure 1 shows a typical schematic diagram of an IGC system for infinite dilution studies used by the author.

To undertake work at high solute concentrations – finite concentration (FC) work – much more complex experimental instrumentation must be employed. The main feature of FC studies is the need to be able to generate both simple, and sometimes complex, concentration profiles of multiple solutes at concentrations, perhaps as high as P/P_0 of 0.95. This necessitates the generation of solute vapours with very stable concentration profiles. Condor and Purcell, amongst other workers, have developed appropriate GC systems to undertake such studies. Current commercial systems incorporate similar instrumental approaches as well as other experimental refinements.

Theory

IGC methods fall into two primary categories. The most common case is infinite dilution (ID) studies in which the solute concentration is low, normally less than 0.01 P/P_0. In this case the solute molecules behave independently and retention behaviour is thus in the Henry's law region. At higher concentrations, when solute–solute interactions become significant, then Henry's law is no longer valid and we refer to FC techniques. These later methods require special experimental techniques as well as complex data analysis.

Infinite Dilution

IGC studies under ID conditions represent over 95% of all IGC papers published in the last 10 years. Subsequently this section will especially highlight the ID approach.

Figure 2 shows four overlaid chromatograms obtained for alkane vapour species interacting with a GC column packed with crystalline fibres at 40°C under conditions of infinite dilution. The quantity t_M is the time for an inert non-interacting species to sweep through the packed column. This time is known as the experimental dead time and is typically measured using methane or nitrogen. This retention time t_M, multiplied by the carrier gas flow rate, F, approximates the dead volume, V_M, within the system. This dead volume consists of the internal volume of the instrumentation plumbing as well as dead space within the sample column.

As the hydrocarbon chain length increases, so does the ability of the solute species to interact with the fibre surface. This results in increasing retention times for the solute molecules. This trend is clearly shown in the peaks shown for hexane through octane. The increased residence time in the GC column results in broader and less intense solute peaks due to increased longitudinal diffusive broadening. The peaks nevertheless maintain their Gaussian shape.

The retention time, t_R, per unit of sample mass for an adsorbing solute vapour allows the net retention volume, V_N, to be determined using eqn [1]:

$$V_N = jt_R F(T/273.15) - jt_M F(T/273.15) \qquad [1]$$

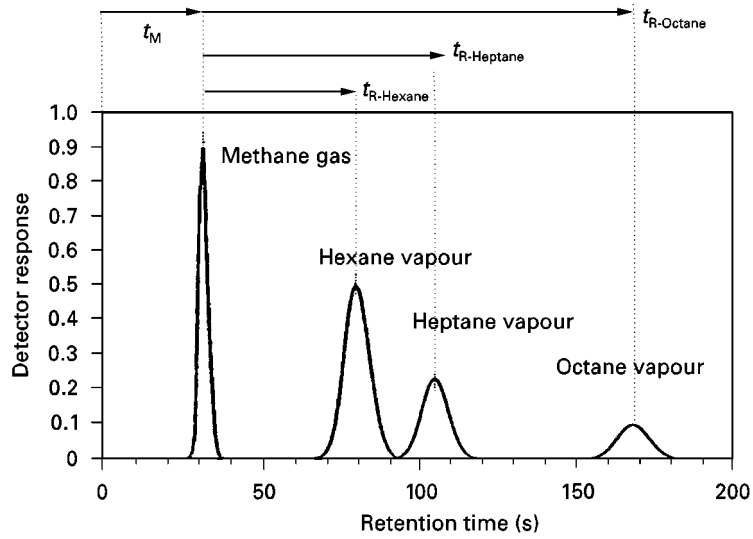


Figure 2 Overlaid chromatograms for alkane vapours on crystalline fibre surface.

where F is the carrier gas flow rate, T is the column temperature, t_M is the dead time and j is a correction term allowing for the pressure changes along the column.

The retention process for the solute with the stationary phase is determined by the solute partitioning between the stationary and mobile phases at the relevant temperature, pressure and concentration. For the case in which the retention process is due to solid–vapour adsorption, solute partitioning between the mobile and stationary phases is given by the appropriate adsorption isotherm. At low solute concentrations ($< 0.01P/P_0$) the adsorption isotherm is typically linear and this region is commonly described as the Henry's law region. In this region solute molecules adsorbing on to a surface are independent and nearest neighbour interactions are not significant. Gaussian-shaped chromatograms, as shown in Figure 2, result in the case of adsorption in the Henry's law region.

In this linear region of the adsorption isotherm, the net retention volume V_N may be related directly to the surface area of the sample A and the partitioning coefficient K_S in the case of surface retention of the solute:

$$V_N = AK_S \qquad [2]$$

In the case in which both surface and bulk retention mechanisms operate, we must modify eqn [2]:

$$V_N = AK_S + VK_B \qquad [3]$$

where the second term relates to bulk sorption into a volume V with a solubility K_BK_S is also the slope of the adsorption isotherm at infinite dilution and is simply defined as the ratio of the solute concentration q in the stationary phase to the solute concentration c in the mobile phase:

$$K_S = q/c \qquad [4]$$

If a dynamic experimental technique is being used to study equilibrium processes, certain precautions need to be performed to confirm the equilibrium nature of the retention data. The simplest and most useful tests to perform are experiments with at least two different flow rates to confirm that the V_N is independent of the carrier gas flow rate.

It is thus apparent that the net retention volume V_N is directly proportional to the slope of the adsorption isotherm and thus the equilibrium constant for the adsorption process. Consequently, standard thermodynamic analysis may be applied to the data. For example, from the temperature-dependent partitioning coefficient K_S the heat of adsorption ΔH_A° using eqn [5] may be determined. Choice of appropriate standard states for the adsorbed species allows both free energies of adsorption ΔG_A° and entropies of adsorption ΔS_A° to be determined as well:

$$q_d = -\Delta H_A^\circ = \mathrm{R}\,\mathrm{d}\,(\ln K_S)/\mathrm{d}(1/T) \qquad [5]$$

$$\Delta G_A^\circ = -\mathrm{R}T\ln(K_S p_{s,g}/\pi_s) \qquad [6]$$

$$\Delta S_A^\circ = -(q_d + \Delta G_A^\circ)/T \qquad [7]$$

A study of V_N as a function of temperature thus allows a detailed study of surface adsorption thermodynamics to be undertaken.

DropBooks

Measuring the retention behaviour of a series of alkane probes allows the dispersive (long range) component of the surface energy of the surface, γ_s^d to be estimated. By estimating the change in retention volume as one increases the size of the alkane probe, the differential free energy of adsorption for an imaginary $-CH_2-$ species can be determined. Using the assumption that an infinite surface of $-CH_2-$ groups is equivalent to a poly(ethylene) surface and with the use of the Fowkes' geometric mean work of adhesion analysis, γ_s^d may be estimated using eqn [8]:

$$\gamma_s^d = (4/\gamma_{s-v})((\Delta G_A^{CH2})/(Na_{CH2}))^2 \qquad [8]$$

where N is Avogadro's constant, a_{CH2} is the area of a $-CH_2-$ group and $\gamma_{s\text{-}v}$ is the surface energy of polyethylene. This simple ratio measurement has become very popular, not least because there is no need to know the exact surface area for the sample.

The above physicochemical properties represent some of the basic IGC measurement types. There exists an extensive range of much more complex analyses which are beyond the scope of this article, including retention by bulk rather than surface retention mechanisms. Other methods include:

1. acid–base interaction constant–donor/acceptor numbers
2. free energies for specific chemical interactions
3. polymer–polymer (Flory–Huggins) interaction constants
4. solubility constants
5. diffusion constants
6. glass transition temperature of polymeric materials

Finite Concentration

Though very little work has been published using FC techniques in the past 10 years, there exists a substantial body of research using these approaches from the preceding 20 years. This work has proven the power and utility of these IGC methods. Like ID, FC is not simply a method but rather a family of experimental approaches linked simply by the use of high solute concentrations. Unlike ID, however, the shapes of the FC chromatograms are rarely Gaussian, but rather take on very complex and nonsymmetrical shapes. Conder and Young's book is still the definitive review of FC methods and should be studied for more detail (see Further Reading).

The fundamental equation from which FC work is based is given below:

$$V_N = A(1 - jy_0)d_q/d_c \qquad [9]$$

where y_0 is the mole fraction of solute in the gas phase at the column inlet and d_q/d_c is the slope of the adsorption isotherm at concentration c.

In this section a brief review of the major FC methods will be provided as well as a general list of the major classes of information which can be determined using FC methods.

The simplest FC method is known as the frontal analysis (FA) approach. In this case a step change in solute concentration is introduced into the IGC column. This concentration boundary will migrate along the column and the time at which the boundary is seen by the detector (minus dead time) will depend upon how much such solute is adsorbed by the stationary phase. A knowledge of the solute concentration and the carrier gas flow rate allows the amount of solute adsorbed to be determined. By undertaking this measurement at differing solute concentrations, an adsorption isotherm may be determined.

Another useful technique is the frontal analysis by a characteristic point (FACP). In this case the shape of the boundary produced by a step change in concentration is analysed. The shape of the tailing of this FC chromatogram can be analysed to provide an adsorption isotherm from one chromatogram via recourse to various analyses based around eqn [9].

For both FACP and FA, very specially modified GC equipment must be used. These modifications are nontrivial and have in turn limited the recent use of these methods. One of the most common FC methods reported in the literature is elution of a characteristic point (ECP). The popularity of this method is simply because it can be undertaken with a standard GC injection system. The technique involves injecting a solute, typically a liquid in one large injection, down the IGC column. The resulting large solute peak will migrate along the column, resulting in the production of a highly nonsymmetrical peak. Analysis of the boundary shape based on eqn [9], not unlike the FACP methods, can allow the adsorption isotherm to be determined from a single or a family of chromatograms.

The final major class of FC techniques is elution on a plateau (EP). In this technique a steady-state concentration profile is established along the IGC column. With an essentially constant concentration profile along the column, a small positive or negative variation in concentration is introduced and the time for the perturbation to propagate along the column is determined (**Figure 3**). This net retention volume will correspond to the K_S for the plateau concentration c under investigation. By undertaking experiments at different concentrations, an adsorption isotherm may be accurately constructed. This method has the major

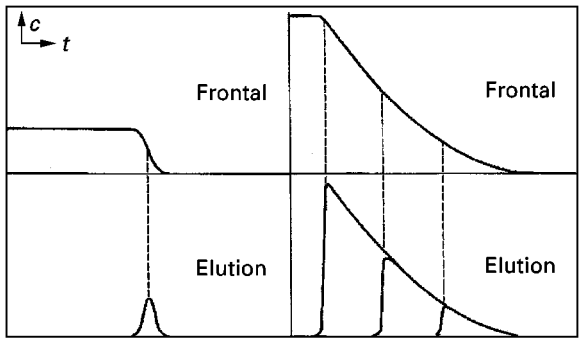


Figure 3 The relationship between frontal and elution chromatograms (after Conder).

advantage over other FC methods that the experiment is undertaken under conditions of essentially constant solute concentration.

Finite concentration methods can be used to determine the following:

1. adsorption isotherms
2. competitive adsorption phenomena
3. porosity and diffusion
4. total uptake/break-through profiles

Applications

Fibres and Filler Particles

The last 20 years have seen a substantial amount of research published on the surface characterization of fibre and filler particles. Invariably these materials are for incorporation in advanced composite materials for which the interfacial properties are known to depend on the surface properties of the reinforcing entities. Measurements of the thermodynamics of adsorption for both weak and strong adsorbing probes are well established for carbon, glass, aramid, cellulose and polyethylene fibres. In many cases their acid–base properties have also been reported. Many high energy inorganic particulate materials have also been investigated, including silica, activated carbon, alumina, bentonite and calcium carbonate. In many cases surface properties have been investigated as a function of heat treatments, surface chemical modifications as well as comminution operations such as milling. Most studies reported have used ID techniques, though FC techniques are also reported periodically.

Pharmaceuticals

The last 5 years have seen a very rapid rise in the interest of the pharmaceutical industry in the use of IGC for the characterization of pharmaceutical materials. The importance of solid dosage forms and the rapid development of novel and complex approaches to solid-state drug delivery have fuelled this interest. Work has already been reported for highly crystalline materials including α-lactose monohydrate, salbutamol sulfate, caffeine, theophylline and microcrystalline cellulose. These studies have focused on changes in surface energies associated with these materials using ID techniques. Such IGC work has already been demonstrated to be a valuable technique for quantifying batch-to-batch variations in pharmaceutical powders not readily, if at all, identifiable using any other experimental approach. The development of IGC instrumentation with multiple solute capabilities has led to work being recently reported for the surface energy of pharmaceutical powders as a function of relative humidity. Such data are also important for understanding practical storage and stability behaviour of pharmaceutical materials. A rapid expansion of work in this area can be expected over the next few years.

Food

IGC work on food materials has been very sporadic during the last 10 years. In many ways this reflects the complex and multicomponent nature of these materials. However, some trends are becoming apparent in this industry. Use of IGC in combination with mass spectroscopic techniques shows great promise for determining the evolution of volatile flavour species from food systems. The ability of IGC to be used for small molecule/polymer solubility has led to the increasing use of IGC for studying base food materials such as starch.

Polymers

Recent highlights include the use of IGC for measuring the permeability of packaging materials to gases and other small solute molecules. Techniques have also been developed for determining the diffusion constants for small molecules, especially for capillary columns coated with polymeric materials. These studies highlight some of the most complex IGC phenomena when both surface and bulk retention mechanisms are operative. Use of IGC to measure the glass transition temperature (T_g) for polymeric materials still attracts significant research interest. IGC is especially sensitive to such a transition due to a change in the retention mechanism from surface dominated below T_g to bulk retention above T_g. T_g has also been measured for thin polymeric coatings which cannot be easily analysed using traditional thermal techniques. Work has also been reported on mesophase transitions for liquid crystalline polymers.

DropBooks

Porous Materials

Porous materials are one of the most complex materials to analyse by any technique, including IGC. This complexity is due to the combination of heterogeneous surface sites and an intricate system of internal and external surfaces. Progress has been made in developing methods for estimating surface basicity and acidity as well as deriving adsorption energy distribution functions. The ability to differentiate solute adsorption due to micropore filling versus surface adsorption has been demonstrated using IGC. This ability allows the true external surface area to be estimated, which is difficult to accomplish with traditional static techniques. Developments in the characterization of these materials have been facilitated by the use of traditional IGC methods combined with thermal ramped desorption approaches which allow information on a wide range of adsorption energies to be determined.

Other Materials

Work has been reported on the use of IGC to characterize coal, sand, conducting polymers, soils and crude oils.

Conclusions

IGC has been shown to be a powerful technique for studying physicochemical interactions between solutes and solid-state materials, especially those at the surface. Indeed, the more extensive use of the technique has clearly been hampered by the lack of commercially available IGC equipment during the past 30 years. Though the number of techniques for surface characterization has increased substantially in the last 20 years (SIMS, XPS, etc.), most of these methods do not provide thermodynamic but rather analytical information. The realization that thermodynamic information about solid-state–solute interactions is important and the very recent advent of commercial IGC instrumentation is likely to result in a significant increase in research using IGC during the next 10 years.

Acknowledgements

Discussions with Dr D. Fetsch and Dr F. Thielmann are gratefully acknowledged.

See also: **III / Reverse-Flow Gas Chromatography.**

Further Reading

Al-Saigh ZY (1997) The characterization of polymer blends by inverse gas chromatography. *Trends in Polymer Science* 5: 97–102.

Conder CL and Young CL (1979) *Physicochemical Measurement by Gas Chromatography*. Chichester: John Wiley.

Kiselev AV and Yaskin YI (1969) *Gas-Adsorption Chromatography*. New York: Plenum Press.

Lloyd DR, Ward TC and Schreiber HP (eds) (1989) *Inverse Gas Chromatography*. ACS Symposium Series 391. Washington: American Chemical Society.

Mukhopadhyay P and Schreiber HP (1995) Aspects of acid–base interactions and the use of inverse gas chromatography. *Colloids and Surfaces* 100: 47–71.

Papirer E and Balard H (1999) Inverse gas chromatography: a method for evaluation of the interaction potential of solid surface. In: Pefferkorn E (ed.) *Interfacial Phenomena in Chromatography*, pp. 145–171. New York: Marcel Dekker.

Pefferkorn E (ed.) (1999) *Interfacial Phenomena in Chromatography*. New York: Marcel Dekker.

Voelkel A (1996) Inverse gas chromatography in the examination of acid–base and some other properties of solid materials. *Studies in Surface Science and Catalysis* 99: 465–477.

Williams DR (1990) Inverse gas chromatography of fibres and filler particles. In: Ishida H (ed.) *Controlled Interfaces in Composite Materials*, pp. 219–232. New York: Elsevier.

Williams DR (1994) Inverse gas chromatography. In: Ishida H (ed.) *Characterisation of Composite Materials*, pp. 80–104. Boston: Butterworth-Heinemann.

PEPTIDES AND AMINO ACIDS: CAPILLARY ELECTROPHORESIS

See **III / AMINO ACIDS AND PEPTIDES: CAPILLARY ELECTROPHORESIS**